Figure 1

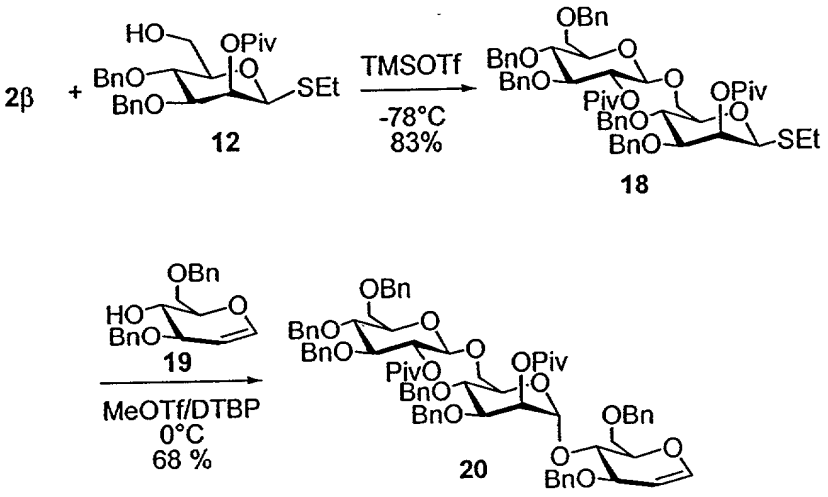
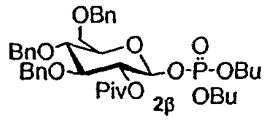
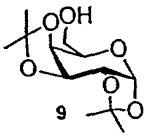
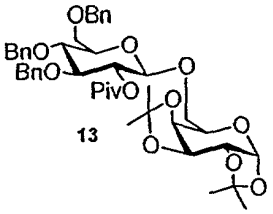
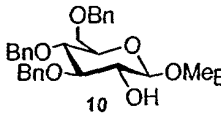
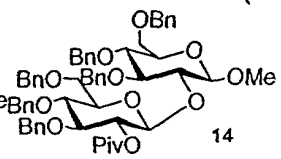
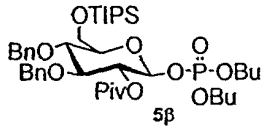
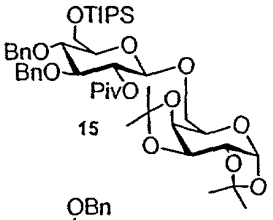
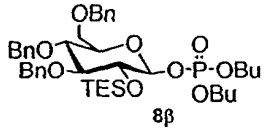
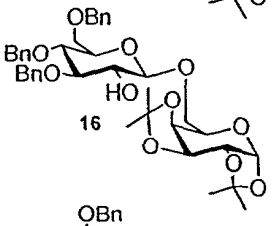
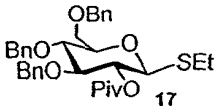
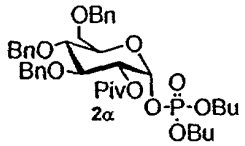

2β
HO
OPiv
BnO
BnO
SEt
12
TMSOTf
-78°C
83%
OBn
BnO
BnO
PivO
OPiv
BnO
BnO
SEt
18
OBn
HO
BnO
19
MeOTf/DTBP
0°C
68 %
OBn
BnO
BnO
PivO
OPiv
BnO
BnO
OBn
O
BnO
20

Figure 2

Table 2. Glycosylations Using Glycosyl Phosphates and Trimethylsilyltriflate.[a]

Entry	Glycosyl Donor	Glycosyl Acceptor	Product	Yield
1	 2β	 9	 13	94
2	2β	 10	 14	83
3	 5β	9	 15	82
4	 8β	9	 16	71
5	2β	 11	 17	90
6[b]	 2α	9	13	87
7[b]	2α	10	14	73
8[b]	2α	11	17	70

[a]Glycosylations were carried out with 1.2 equiv donor, 1.0 equiv acceptor and 1.2 equiv TMSOTf in dichloromethane at -78°C. [b]Reaction was carried out at -20°C.

Figure 3

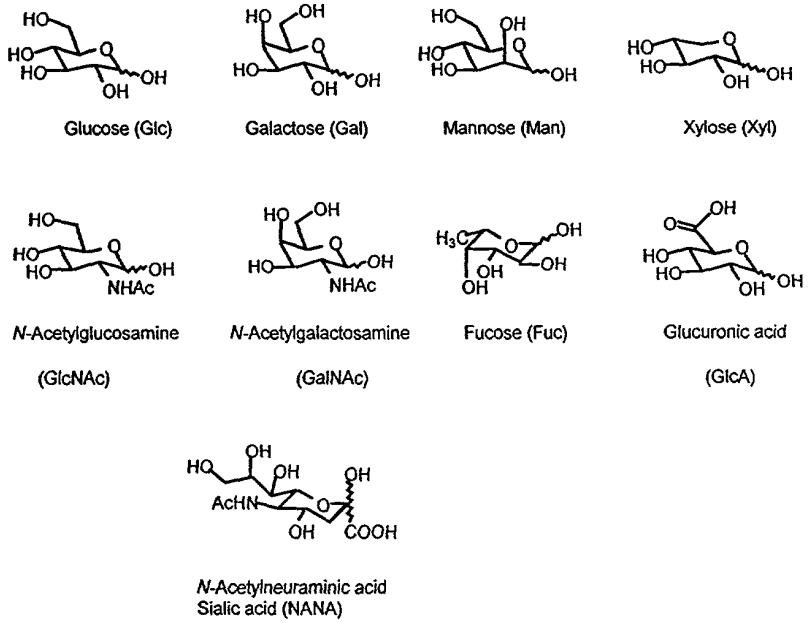
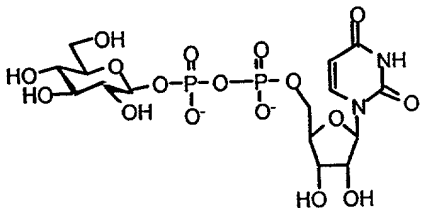
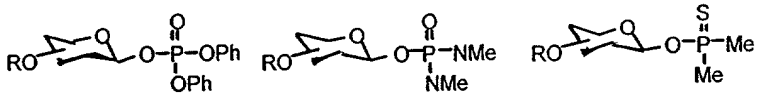

Glucose (Glc)
Galactose (Gal)
Mannose (Man)
Xylose (Xyl)
N-Acetylglucosamine
(GlcNAc)
N-Acetylgalactosamine
(GalNAc)
Fucose (Fuc)
Glucuronic acid
(GlcA)
N-Acetylneuraminic acid
Sialic acid (NANA)

Figure 4



UDP-Glucose

Figure 5



1 2 3

5

Figure 6

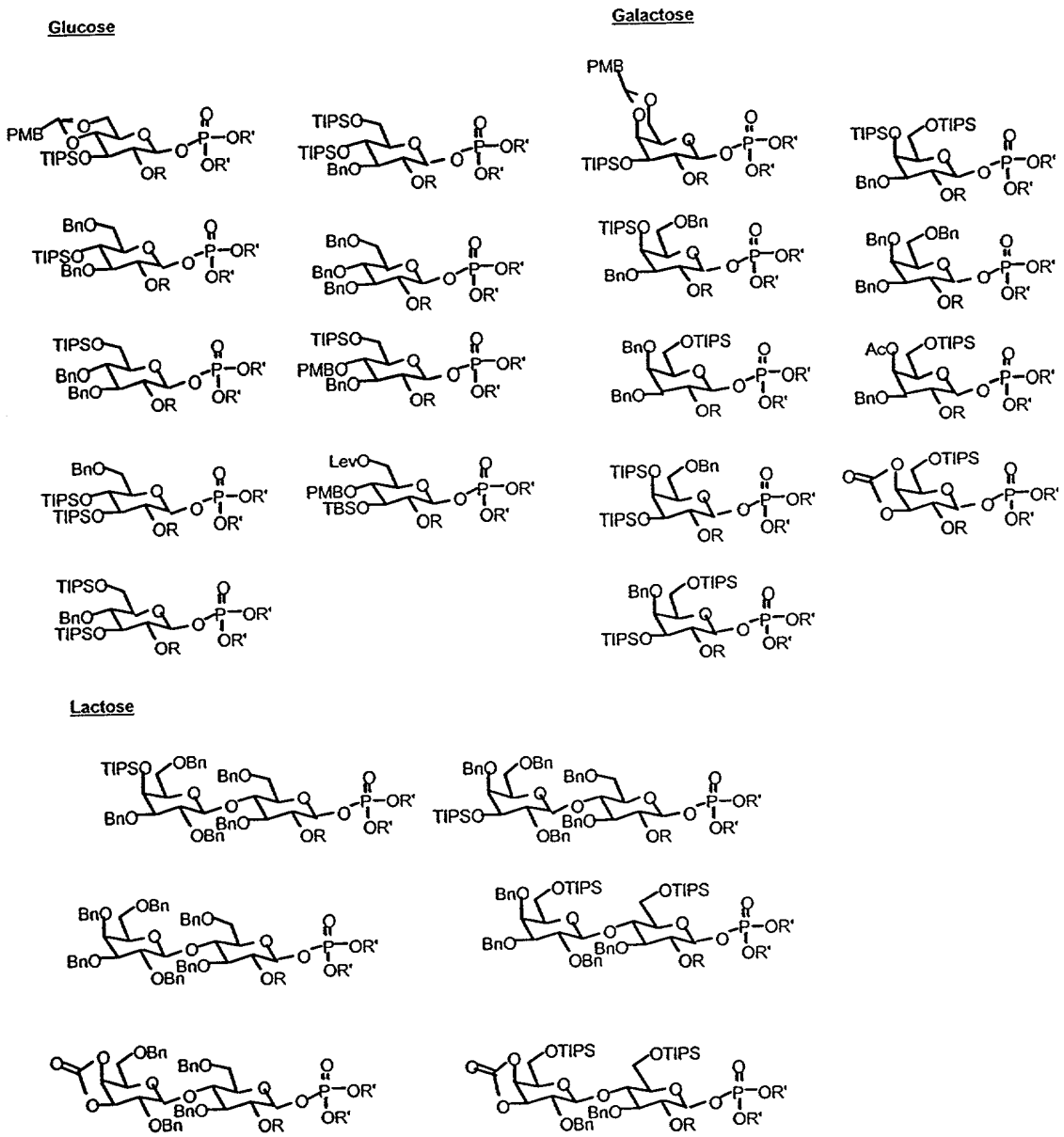
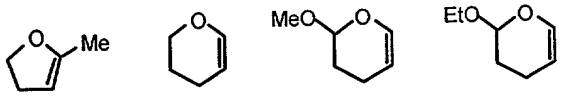

Glucose
Galactose
Lactose
PMB
TIPSO
BnO
OR
OR'
P
O
TIPSO
BnO
OR
OR'
BnO
TIPSO
BnO
OR
OR'
BnO
BnO
OR
OR'
TIPSO
BnO
OR
OR'
TIPSO
PMBO
BnO
OR
OR'
BnO
TIPSO
OR
OR'
LevO
PMBO
TBSO
OR
OR'
TIPSO
BnO
TIPSO
OR
OR'
PMB
TIPSO
OR
OR'
TIPSO
OTIPS
BnO
OR
OR'
TIPSO
OBn
BnO
OR
OR'
BnO
OBn
BnO
OR
OR'
BnO
OTIPS
BnO
OR
OR'
AcO
OTIPS
BnO
OR
OR'
TIPSO
OBn
TIPSO
OR
OR'
OTIPS
O
OR
OR'
BnO
OTIPS
TIPSO
OR
OR'
TIPSO
OBn
BnO
BnO
OBn
OR
OR'
BnO
OBn
BnO
TIPSO
BnO
OBn
OR
OR'
BnO
OBn
BnO
BnO
OBn
OR
OR'
BnO
OTIPS
OTIPS
BnO
BnO
OBn
OR
OR'
OBn
BnO
BnO
OBn
OR
OR'
OTIPS
OTIPS
O
BnO
OBn
OR
OR'

Figure 7



5

Figure 8

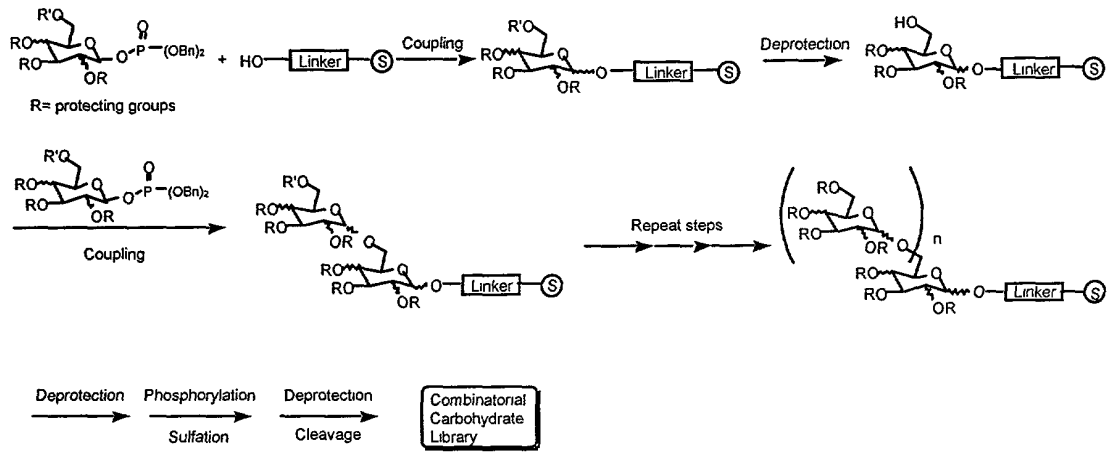
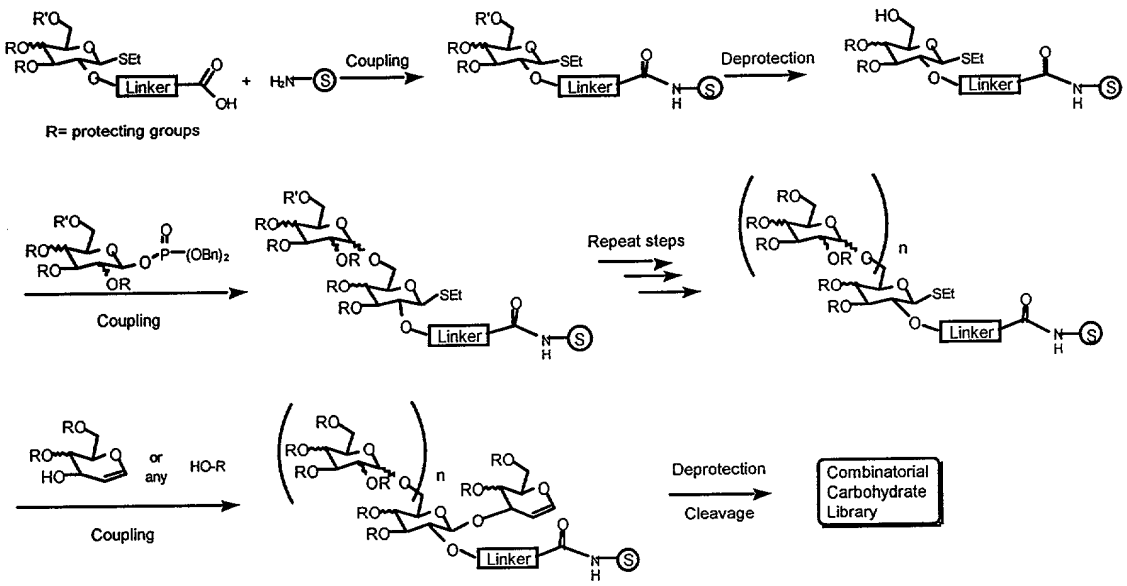

R'O
RO
RO
OR
O
P
(OBn)2
+
HO
Linker
S
Coupling
Deprotection
HO
R= protecting groups
Coupling
Repeat steps
n
Deprotection
Phosphorylation
Sulfation
Deprotection
Cleavage
Combinatorial
Carbohydrate
Library

Figure 9


R'O
RO
RO
SEt
Linker
OH
+ H2N
S
Coupling
Deprotection
HO
R= protecting groups
O
P
(OBn)2
OR
Repeat steps
n
or
any
HO-R
Coupling
Deprotection
Cleavage
Combinatorial
Carbohydrate
Library